near the metal. Furthermore, the finite size of the target precludes observation of a minimum energy greater than zero on geometrical grounds.

The discussion of theory included here is admittedly sketchy. It is meant to show the consistency of the theoretical results with the conclusions concerning the state of the tantalum surface and its work function demanded by the experiment. A detailed account of the theory, including conclusions stated here without proof, is forthcoming.

The author wishes to acknowledge with thanks the discussions with his colleagues, J. A. Hornbeck, K. G. McKay, J. P. Molnar, and A. H. White, the efforts of H. W. Weinhart in design and supervision of construction of the experimental apparatus, and the technical assistance of F. J. Koch.

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Reversible Bleaching of a Band in the Absorption Spectrum of Diamond

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When diamonds which show the absorption band in the near ultraviolet, characteristic of blue fluorescing samples, are exposed to neutron bombardment, a continuous absorption slowly rising toward shorter wavelength is superimposed upon the band. Heating such a diamond to temperatures between 300° and 600°C decreases the continuous absorption and the structure of the band becomes appreciably sharper. Subsequent exposure to light greatly reduces the height of individual peaks in the band, while the continuous absorption at shorter wavelengths is increased. Renewed heating restores the sharp structure of the band and the cycle can be repeated at will. Heating the crystal to 750°C brings the crystal very nearly back into the state before neutron bombardment in which the reversible bleaching cannot be observed. A similar band accompanies the sharp line at 503 mμ that is produced in the absorption spectrum of diamonds by neutron bombardment and heat. The structure of this band is also altered by heating to various temperatures but is not affected by absorption of light.

MOST diamonds of the so-called type I show in their absorption spectra a sharp line at 415.2 mμ and an adjoining band with a number of peaks in the range from 405 to 350 mμ. It has been mentioned in a preceding paper[1] that under certain conditions the intensity distribution within this band can be altered appreciably and reversibly by heating a diamond in the dark to temperatures between 300 and 500°C and then exposing it to violet or near ultraviolet radiation. The phenomenon had been observed only with a diamond which had previously been subjected to neutron bombardment in the Argonne heavy water pile. However, since the band was present in the absorption spectrum before this treatment, it seemed probable that even then it would have exhibited the same behavior which might be connected with the well-known thermoluminescence properties of many diamonds.

In more recent experiments, several diamonds were investigated in which the line and band in the neighborhood of 400 mμ in the absorption spectra before irradiation had a much greater intensity than in the earlier sample. Moreover, the spectra were recorded at the temperature of liquid nitrogen at which temperature the structure of the band is much better resolved than at room temperature. Figure 1, curve a represents the absorption spectrum from 800 to 300 mμ of one of the new diamonds (D46) before any treatment. The line at 415.2 mμ is somewhat distorted on the curves of Fig. 1 because the scanning speed of the recording spectrophotometer was too great for the high intensity and sharpness of the line. Curve a in Fig. 2 represents the region from 420 to 300 mμ of the same spectrum with a tenfold slower scanning speed. The relative intensities of the line and the various band peaks are shown with much better accuracy in this figure.[2] Repeated heating of the diamond to temperatures between 300 and 650°C and subsequent exposure to light did not alter the spectrum in the least. The same result was obtained with another sample (D52). Curves b in Figs. 1 and 2 represent the absorption spectrum of the diamond D46 after 20 hours exposure to neutron bombardment. The absorption spectrum is characterized by a broad band in the orange and a strong increase of absorption below 500 mμ. Since the maximum transmission is located in the neighborhood of 500 mμ, the crystal acquired the well-known blue-green color in transmitted light. The nearly straight line c, obtained as the difference between curves b and a in Fig. 2, proves that, at least in this spectral region, the effect of the pile exposure consists only in the super-

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[1] P. Pringsheim and R. Voreck, Z. Physik **133**, 2 (1952).

[2] On spectrograms obtained by several investigators with spectrographs of higher resolving power, additional fine structure appears in the band, of which only a trace can be recognized in the curves of Figs. 2 and 3. [See P. G. N. Nayar, Proc. Indian Acad. Sci. **A15**, 293 (1942); A. Mani, Proc. Indian Acad. Sci. **A19**, 231 (1944).]

position upon the original band of a continuous and continuously rising absorption without any selectivity. As shown by comparison of curve b of Fig. 2 with curve a of Fig. 3 this continuum is not uniformly reduced by a certain amount when the diamond is heated at 540°C, but simultaneously the band peaks beginning with the one at 393 mμ are relatively enhanced and some of them at least become much sharper, while the line at 415.2 mμ and the first band peak remain essentially unaltered. This is demonstrated very clearly by curve d of Fig. 3, which was obtained as the difference between curve b of Fig. 2 (before heating) and curve a of Fig. 3 (after heating). At the peak wavelengths, 393, 384, 375, and 366 mμ, the decrease in optical density is much smaller than in the other parts of the spectrum. If the crystal, which so far had been kept in the dark, was now exposed for an hour to the radiation of a mercury-H4 lamp,[3] the intensity distribution in the absorption band is altered as indicated in curve b of Fig. 3. Curve c in the same figure, which is almost exactly complementary to curve d, is drawn as the difference between curves a and b of Fig. 3. Curve e of Fig. 3, which represents the difference between curve b of Fig. 2 and curve b of Fig. 3, is again very nearly a straight line. Thus, a part of the continuum produced by neutron bombardment is bleached out by heating and irradiating with light while by heat alone, in addition to the general bleaching, the band peaks below 403 mμ are enhanced. The relatively larger intensity loss which heating produces in the continuum below 340 mμ is recovered in the light bleaching process.

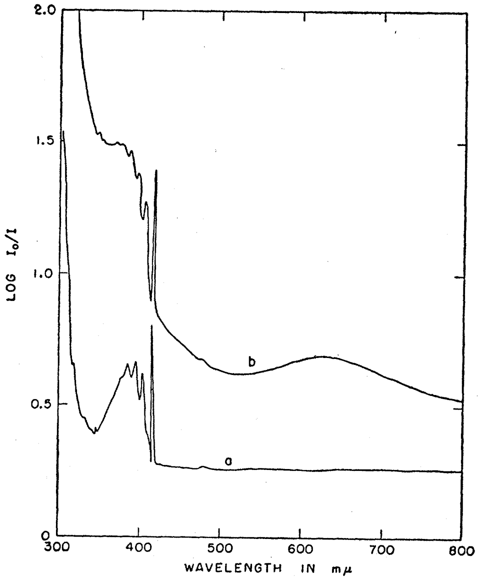

FIG. 1. Absorption spectrum of diamond D46 recorded at −190°C. a. Before treatment; b. after exposure in the pile

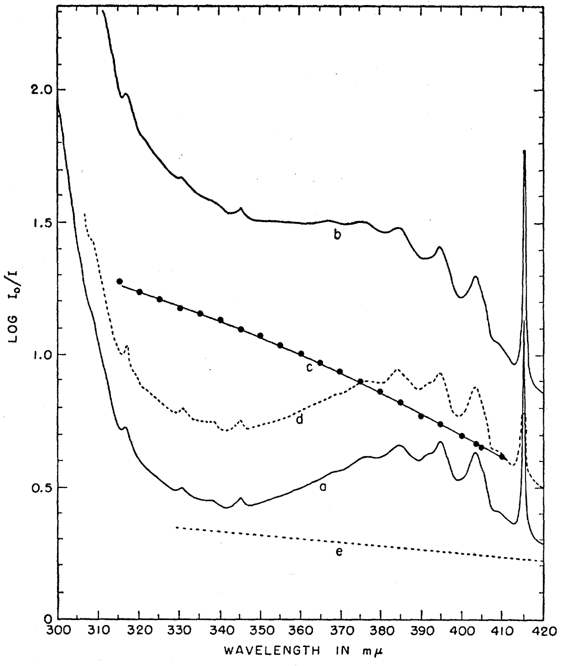

FIG. 2. Absorption band of diamond D46 below 420 mμ recorded at −190°C. a. Before treatment; b. after exposure in pile; c. difference b−a; d. after 20 hours at 750°C; e. difference d−a.

The temperature range in which this effect is produced lies between 300 and 650°C, with an optimum between 450 and 550°C. The case represented in Fig. 3 relates to heating at 540°C. Almost identical sets of curves were obtained with another irradiated diamond (D44) after heating it to 450°C. A second heat treatment at the same temperature reproduced exactly the same behavior. A third diamond (D19) underwent the entire cycle of treatments five times: heating to 350°C, bleaching with light and reheating, every time with identical results. It thus appears that when a pile-irradiated diamond has been heated for one hour to a certain temperature, additional heating at the same temperature does not alter its optical properties any further, except to enhance the various band peaks, and this effect disappears again under exposure to light. The bleaching is quite as effective when the crystal is kept at the temperature of liquid nitrogen as it is at room temperature. Heating to temperatures as low as 300°C or as high as 650°C produces the same phenomenon, but the sharpening and enhancement of the band peaks are less pronounced. This is no longer true, when the diamond is heated to 750°C. In this case the crystal is converted directly into the state represented by curve d of Fig. 2. The difference between this curve and curve a is given by the slowly rising straight line e in Fig. 2 which represents the small remainder of the continuum produced by the neutron bombardment. Exposure to light does not alter this state further.

The line at 415.2 mμ and the first main band peak at 403 mμ are practically unaffected by the treatment

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[3] It has been shown that the green-yellow lines of the mercury arc are ineffective and that the violet and near ultraviolet lines are responsible for the bleaching. (See reference 1.)

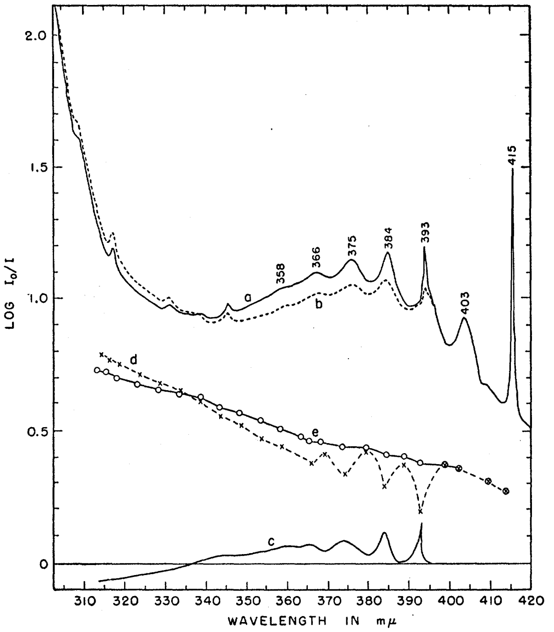

FIG. 3. Absorption band of diamond D46 below 420 mμ recorded at −190°C. a. After 20 hours in pile and 1 hour at 540°C in the dark; b. after 1-hour exposure to Hg arc light; c. difference a−b; d. difference between b of Fig. 2 (after pile exposure) and a of Fig. 3 (after heating in dark); e. difference between b of Fig. 2 (after pile exposure) and b of Fig. 3 (after heating and light bleaching).

described above. The line corresponds almost certainly to a purely electronic transition and the adjoining band originates from transitions to various vibrational levels of the excited electronic state. The spacing of the peaks is of the order of magnitude occurring also in the infrared and Raman spectra of diamond. An exact coincidence is not to be expected because these vibrational frequencies belong to different electronic states. Moreover, the peaks are not characteristic of transitions to a single series of vibrational levels but to several overlapping series. Even the incompletely resolved spectra represented by Figs. 2 and 3 show this. The sharpening of the peak at 393 mμ is clearly due to the disappearance of a weaker component forming a shoulder on the long wavelength side of the main peak. The complex formed by the line and the band is always weak. Even in the spectra of samples which show it with relatively great intensity the absorption at the center of the band seldom exceeds 10 cm^{-1}, with a half-width of about 0.5 ev. This means that either the corresponding electronic transition occurs in all atoms of the diamond lattice with an oscillator strength of about 10^{-8} or that a relatively small number of "centers" with an appreciably greater oscillator strength are responsible for the absorption. The fact that the intensity of the band differs so widely in various samples is definitely in favor of the second assumption.

This does not mean necessarily that the line and band are due to the presence of impurities. It might quite as well be possible that local irregularities in the lattice make possible an electronic transition in the carbon atom which otherwise is strictly forbidden.[4] However this may be, it seems reasonable to assume that the absorption of the line and band is localized in certain "centers" which may be called 415-centers.

The optical properties of diamond are altered in several respects by neutron bombardment. Among other phenomena, a continuous and continuously rising absorption band is produced in the violet and near ultraviolet. This must be due to the creation of some sort of perturbations, such as interstitial atoms, vacancies, etc., which, macroscopically, are uniformly distributed throughout the crystal. There is no reason to suppose that these perturbations are directly connected with the existence of the 415-centers, since they are formed with equal intensity in diamonds which have little or no intensity in the 415-mμ line and band. Nevertheless, the presence of these perturbations in the vicinity of the 415-centers alters their reaction to the influence of heat.

The increase in the relative intensity of certain peaks in an absorption band reveals the fact that the transitions to certain vibrational levels of the excited electronic state have become more probable, while others—and in our case also transitions into a nonquantized continuum—have become less probable. This can be the consequence of a small shift in the relative position of the configurational potential curves due to changes in the arrangement of the neighboring perturbations. The normal arrangement of the perturbations is restored by irradiation with light. It is not possible to ascertain whether the light absorption occurs in the 415-centers or in the perturbation continuum, because the latter is superimposed on the former. However,

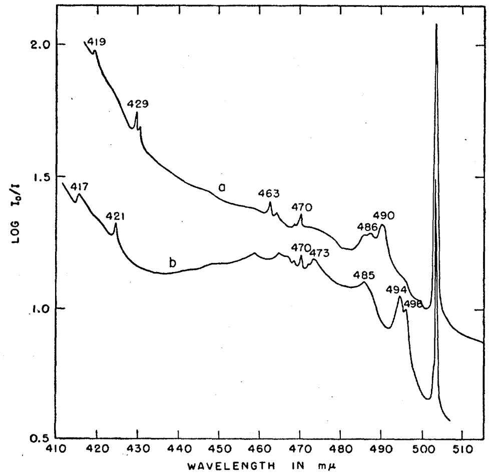

FIG. 4. Absorption band of diamond D14 below 510 mμ recorded at −190°C. a. After prolonged pile exposure and heating at 540°C; b. after 1 hour at 775°C.

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[4] G. N. Ramachandran and V. Chandrasekhar, Proc. Indian Acad. Sci. A24, 176 (1946).

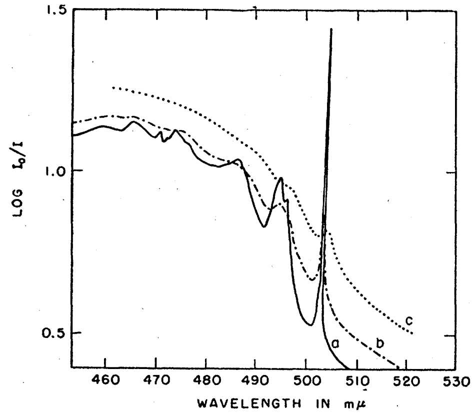

FIG. 5. Absorption band of diamond D14 after additional heating at 450°C. a. Recorded at −190°C; b. recorded at −78°C; c. recorded at +25°C.

since the effect is only observed in the neutron bombarded crystals and vanishes when the continuum has practically disappeared after heating to 750°C, the second assumption is probably correct.

The absorption spectra of some diamonds are known to contain a second sharp line at 503 mμ, and this line too is accompanied by a band at its short wavelength side. None of the 52 industrial diamonds investigated in this laboratory[5] exhibited this line before undergiong neutron bombardment. As observed first by Dugdale,[6] however, a line of apparently the same wavelength arises in the absorption spectrum of diamonds which have been exposed to neutron bombardment and subsequently heated at temperatures of about 300°C. Although the line could be produced by suitable treatment in the spectra of all diamonds investigated so far, it appears that samples of the type I variety with a low intensity 415-mμ line and adjacent band show the strongest response in the production of the line at 503 mμ. Since the region around 500 mμ in the diamond absorption spectrum is least affected by pile exposure, appreciably longer exposures are necessary in this case than were used in the experiments described in the first part of this paper. On the other hand, after such a strong neutron bombardment the crystals withstand heating to much higher temperatures before being completely bleached. When produced by heating a pile-irradiated diamond to temperatures between 300 and 350°C, the line at 503 mμ, accompanied by only one weak broad band peak at 490 mμ, is clearly visible on a continuous background in spectra recorded at room temperature, as shown in Figs. 3 and 4 of the earlier paper.[1] After heating to 400°C or more the line is practically invisible if the spectrum is again recorded at room temperature, but it reappears with great intensity and great sharpness in the spectrum recorded at −190°C. In addition to its main peak which is still located at 490 mμ, the band now exhibits a number of secondary peaks. This is shown in curve a of Fig. 4 which represents the spectrum of diamond D14 after repeated pile exposure and heating to temperatures below 600°C. Curve b of Fig. 4 reproduces the spectrum of the same sample after it had been heated for an hour to 775°C. The intensity of the line and the background is reduced by about 20 percent, and the structure of the band is altered appreciably. The most striking alteration in the band structure is the appearance of a new double peak at 495 mμ and the almost complete disappearance of the peak at 490 mμ. This change in the intensity distribution is not reversed when the diamond is exposed to light. Curve a of Fig. 5 is very nearly a repetition of curve b in Fig. 4. It was obtained with the same diamond after heating it once more for one hour at 450°C. Curves b and c of Fig. 5 illustrate how the line and band are almost totally submerged under the continuum when the temperature at which the spectrum is recorded is raised to −78° and −25°C, respectively.[7]

The intensity of the line at 503 mμ can be enhanced appreciably by successive periods of neutron bombardment and heat treatment, but even the highest intensities obtained so far do not exceed the order of magnitude mentioned in connection with the line at 415 mμ. Thus the line at 503 mμ must probably be ascribed also to a normally forbidden transition in relatively few centers which, in this instance, are not present in the crystal before exposure in the pile. An interpretation of the various observations concerning the 503-mμ line and the adjoining band would require the introduction of numerous arbitrary assumptions with respect to the perturbations produced in the lattice and their influence on the centers responsible for the line. Such a tentative interpretation would practically be merely a repetition of the description of the observed facts with other words.

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[5] Most of these diamonds were returned to Super-Cut, Inc., after a cursory inspection of their absorption spectra, while only seven samples were selected because of their specific qualities for further treatment. I want once more to thank D. A. Trescott of Super-Cut, Inc., for his kind help in this matter.

[6] R. A. Dugdale, Harwell Report AERE-N/*PC*-15, 1950 (unpublished); P. Pringsheim, Argonne National Laboratory Report ANL-4797, 1951 (unpublished).

[7] Almost identical behavior is shown by a line which can be produced in the absorption spectrum of lithium fluoride by exposure to x-rays and subsequent irradiation with short wavelength ultraviolet light [C. F. Delbecq and P. Pringsheim, J. Chem. Phys. **21**, 794 (1953)].